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1,3,5,7-TETRATHIACYCLOOCTANE TETRAANION

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The tetracarbanion of 1,3,5,7 tetrathiacyclooctane has been prepared by the action of butyl lithium on the parent heterocycle. This molecule is representative of a novel cyclic species in which the orbital symmetry allows each atom to contribute one atomic orbital to form extended π orbitals. Proof of the structure has been demonstrated by the formation of tetradeutero and tetramethyl derivatives.

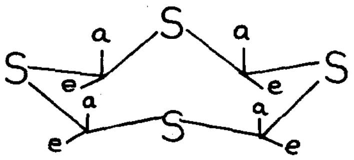
The stabilisation of radicals and anions on carbon atoms adjacent to sulphur is well known and arises as a result of overlap with sulphur d orbitals(1-7). This property is of particular interest in thioacetals, where the carbon atom is flanked by two sulphur atoms, each of which can contribute a d orbital, resulting in increased stabilisation. Thus sulphur stabilised carbanions have been prepared from 1,3-dithiane, 1,3-dithiane-1-oxide(5,8), 2-methyl-1,3-dithiane(9) and have been shown to undergo nucleophilic reactions typical of carbanionic species.

In a recent paper, Bank and Coffen(10) described the preparation of a dianion from 5,7-dimethyl-tetrathiaadamantane and suggested that by extending the thioacetal type of chain (i.e. going from S-C-S to S-C-S-C-S) a more extensive π molecular orbital should be formed. In the present work this argument has been applied to cyclic thioacetals of the general formula $(CH_2S)_n$ in anticipation that the same principles should apply.

The formation of polycarbanions from cyclic polythioacetals of the formula $(CH_2S)_n$ should be possible and in particular when n is even and providing the molecular geometry is favourable, n carbanionic centres should be formed.

In these circumstances the orbital symmetry is such as to allow, in an ideal situation, electrons to be spread over n atomic orbitals to form extensive π molecular orbitals although, in the present example, it is likely that 'island' formation(11) is likely because of non-planarity in the heterocyclic ring. When n is an odd number the sp^3 orbital of the first carbon atom and the d orbital of the last sulphur atom will be of opposite sign and a situation similar to that in the phosphonitrilic compounds(12) will exist. 1,3,5,7 tetrathiacyclooctane, a compound represented by the formula $(CH_2S)_4$, is easily obtained by the reaction of methylene chloride with sodium sulphide. Treatment of this compound with butyl lithium in the presence of an activator such as N,N,N',N'-tetramethyl ethylene diamine in tetrahydrofuran solution yielded the yellow tetracarbanion as indicated by the following data. Quenching of the reaction product with an excess of deuterium oxide yielded 2,4,6,8-tetradeutero-1,3,5,7-tetrathiacyclooctane in 92% yield, as indicated by N.M.R. spectrum. A comparison of the N.M.R. spectra of the starting material and the deuterated product in the presence of equimolar amounts of p-nitrotoluene (internal standard) revealed, in the first case, a ratio of 8:3 aliphatic protons and in the second case a ratio of 4:3, suggesting that one proton of each methylene group had been replaced by deuterium. The high yield of deuterated starting material is indicative of the stability of the tetraanionic species. Treatment of 1,3,5,7-tetrathiacyclooctane with butyl lithium and methyl iodide yielded a mixture of products. These could be separated by preparative gas chromatography into three main components (ca. 80-85% of the total). The first component, representing about 65% of the product was obtained as a crystalline solid. The mass-spectrum showed a molecular ion at mass 240 corresponding to 2,4,6,8-tetramethyl-1,3,5,7-tetrathiacyclooctane (M.W. 240). Other major fragments located at mass-numbers 180,120 and 60 correspond to loss of thioacetaldehyde units. The N.M.R. spectrum, determined in CCl_4, showed a -C-H splitting (quartet) at 5.5T and a $-CH_3$ splitting (doublet) at 8.34T (J = 7 c/s) with intensities in the ratio of 1:3. These data indicate that each of the $-CH_2$ groups has had one proton replaced by a methyl group.

An examination with the use of atomic models suggests that the most stable configuration of 1,3,5,7-tetrathiacyclooctane is the "crown" form in which the bonds are shown schematically below and labelled 'e' or 'a'



Four tetramethyl isomers are possible and the ease with which they can be set up with atomic models is indicated below

i) e,e,e,e - readily constructed

ii) e,e,e,a - restricted rotation of axial methyl group

iii) e,e,a,a, - difficult to accommodate

iv) e,a,e,a - difficult to accommodate

In the absence of other data it is proposed that the most likely isomers of the tetramethyl derivative are i) and ii). The N.M.R. spectrum of the product is consistent with structures i), iii) and iv) but not ii) and in view of the fine crystalline form of the product it is suggested that the compound isolated is all <u>cis</u> - 2,4,6,8-tetramethyl-1,3,5,7-tetrathiacyclooctane.

The second component of the reaction product (<u>ca</u>. 25%) was also isolated as a crystalline solid with a melting point only 1° different from that of the first component. The mass-spectrum revealed a molecular ion at mass 240 suggestive of an isomer of the tetramethyl compound described above. The N.M.R. spectrum showed a nine peak C-H splitting in the 5-6T region and a methyl triplet at 8-8.5T. These absorptions had the relative intensities of 1:3 as expected for a tetramethyl derivative. Closer examination showed that the C-H absorptions consisted of four quartets, one centred at 5.14T, and one at 5.77T and two superimposed at 5.55T. The triplet structure was formed from two superimposed pairs of doublets at 8.31T and 8.43T. There is no ambiguity about the identity of this compound since the N.M.R. spectrum is identical with that expected for compound ii)(see above) i.e. cis, cis, trans-2,4,6,8-tetramethyl-1,3,5,7-tetrathiacyclooctane. The infra-red spectra of the two tetramethyl isomers were almost identical and showed the expected absorptions at 3.4μ ($-CH_3$ stretch), 6.9μ and 7.3μ ($-CH_3$ deformation).

The third component was obtained in very small yield as a viscous liquid which could not be induced to crystallise. The mass-spectrum indicated a molecular ion at mass 226 corresponding to 2,4,6-trimethyl-1,3,5,7-tetrathiacyclooctane. The N.M.R. spectrum showed signals due to -CH (quartet) at 5.6T, $-CH_2-$ (singlet) at 6.0T and $-CH_3$ in the form of two doublets, one at 8.37T and the other of half the intensity at 8.42T. The overall intensities were in the ratio of 3:2:9. The spectroscopic data are consistent with the compound being trans, trans-2,4,6-trimethyl-1,3,5,7-tetrathiacyclooctane.

A logical extension of this work should be an examination of the properties of the dianion from the, so far, unknown 1,3-dithiacyclobutane which represents the lowest number of the series $(CH_2S)_n$ (i.e. n = 2) for which delocalisation might occur.

Spectroscopic data

N.M.R. spectra were run on a Perkin-Elmer (60 m/c) instrument using, where appropriate, tetramethylsilane as an internal standard.

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